Characters of Activated Carbon for Hg Removal of Flue Gas with H_2S and Iron Oxide for Hg Removal of Coal Derived Fuel gas with H_2S

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Introduction

The major anthropogenic sources of mercury emission are coal combustion and municipal waste incineration. However, it is very difficult to remove the mercury compounds, particularly elemental mercury vapor, which is not effectively captured in typical air – pollution control devices. It has been reported that activated carbon, particularly activated carbon impregnated with sulfur, chlorine, and iodine, are effective for Hg removal.[1-4] However, the major drawbacks of activated carbons are high cost, poor capacity, narrow temperature range and slow regeneration and adsorption rates.

We have presented a novel Hg removal method using H_2S and adsorbents.[5,6] This method based on the reaction of H_2S and Hg over adsorbents. Although the reaction mechanism is not well understood yet, but it has been suggested in our previous report that Hg reacts with H_2S and forms HgS.[5] The sublimation point of HgS(cubic) is 446^{o}C. If the reaction (adsorption) between Hg and H_2S over suitable adsorbent (catalyst) occurs at a temperature well below the sublimation point of HgS, then elemental mercury can be removed from the flue gas effectively. In this study, we tried to clarify the removal characters of an activated carbon and an iron oxide for the removal of Hg vapor: The activated carbon was useful for the Hg removal from a combustion flue gas; the iron oxide was useful for the Hg removal from a coal derived fuel gas.

Experimental

Sorbents. Activated Carbon (AC) was purchased from Wako Pure Chemical Co. LTD. The raw material of this activated carbon was coconut shell. The granular active carbon was washed with de-ionized water and calcined for 3h at 300^o in the N_2 flow. The granular AC particles were sieved into an average diameter of 1.0mm. BET surface area measured using liquid nitrogen was ca. 1100m^2/g.
An iron oxide sample was prepared by a precipitation method using a reagent grade $Fe(NO_3)_3.9H_2O$ and NH_3aq at room temperature. The precipitant was washed with de-ionized water and dried for 25h at 110^{o}C under atmosphere. The dried sample contained FeO(OH). BET surface of the sample was ca.200m^2/g.

Apparatus and Procedure. The evaluation of the reactivity of the samples was carried out using a flow-type packed bed reactor under atmospheric pressure. About 0.5 cm^3 or 0.25 cm^3 of the sample particles (diameter: 1.0m.) was set in quartz tube reactor. The reaction temperatures range examined was from 80 to100^{o}C. The reaction for Hg removal of flue gas was carried out with a mixture of Hg (4.8ppb), H_2S (0 or 40ppm), SO_2(0 or 250ppm), CO_2 (13%), H_2O(8%), O_2(5%), and N_2 (balance gas) at 500cm^{3}STP/min (SV:6.0X10^4 h^{-1}). The reaction for Hg removal of coal derived fuel gas commenced when a mixture of Hg(4.8ppb), H_2S(400ppm), CO(30%), H_2(20%), H_2O(8%), and N_2 (balance gas) was fed into the reactor at 500 cm^{3}STP/min (SV:12X10^4 h^{-1}). The measurement of the inlet and outlet concentration of mercury were carried out using a cold vapor mercury analyzer.

Results and Discussion

Character of AC for removal of the flue gas with H_2S.

Effect of the temperature on the Hg removal in the both presence of H_2S and SO_2. As shown in **Figure 1**, there was a suitable temperature: the

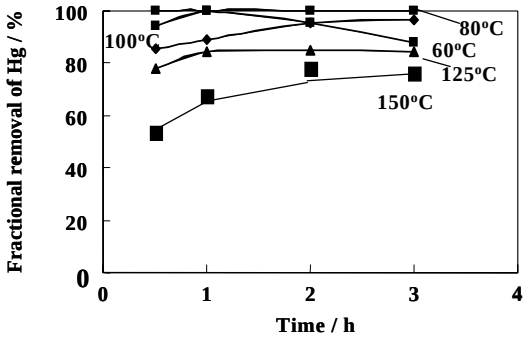

Figure 1. Effect of temperature on the Hg removal.

temperature range was 80 ^{o}C. The reason of this dependency of the temperature on reactivity may be explained by the removal mechanism if the mechanism is clarified.

Effect of the presence of SO_2 and H_2S on the Hg removal

The AC removed a negligible amount of Hg at 150^{o}C in the presence of SO_2 or H_2S. However, in the both presence of SO_2 and H_2S, the AC could remove the considerable amount of the Hg as shown in **Figure 1**. This result may suggest that Claus reaction occurred over the AC and the produced sulfur reacted with the Hg vapor.

$$SO_2 + 2H_2S = S_{ad} + 2H_2O \quad (1)$$
$$S_{ad} + Hg = HgS \quad (2)$$

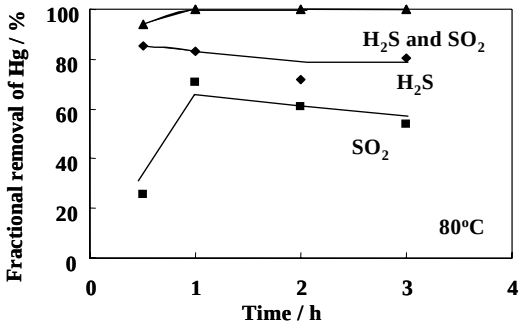

Figure 2 Effect of the presence of SO_2, H_2S and SO_2-H_2S.

As shown in **Figure 2**, the AC could remove a considerable amount of the Hg vapor in the only presence of SO_2 or H_2O at low temperature (80^{o}C),. In the both presence of SO_2 and H_2S, the AC could almost perfectly remove the Hg vapor as shown in Figure1. This result suggests that the mechanism of the Hg removal with AC is different at the low- and the high-temperature. Furthermore, the difference of the mechanism in the temperature range may be a cause of the existence of the suitable temperature for the Hg removal.

Effect of the presence of H_2O on the Hg removal

The presence of H_2O at 100 and 80^{o}C accelerated the Hg removal

with the AC in the both presence of H_2S and SO_2. However, the presence of H_2O at 150°C depressed the Hg removal with the AC as shown in **Figure 3**. This result also suggests that the mechanism of the Hg removal is different at the low and high temperature.

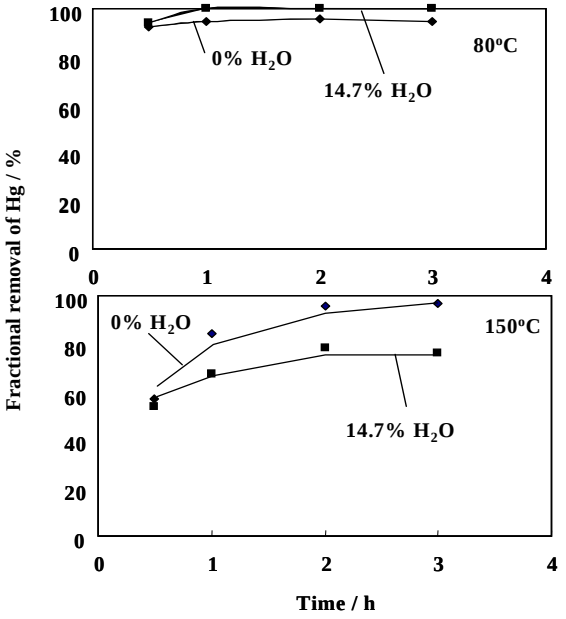

Figure 3. Effect of the presence of H_2O.

Character of the Iron oxide for Hg removal of the coal derived fuel gas with H_2S.

Effect of the temperature on the Hg removal

As shown in **Figure 4**, the activity of the iron oxide for the Hg removal increased with the decrease of the reaction temperature. After use of the iron oxide under the low temperature60 and 80°C, the sample was not changed when it was exposed to the air. However, at the high temperature 150°C, the temperature of the used sample

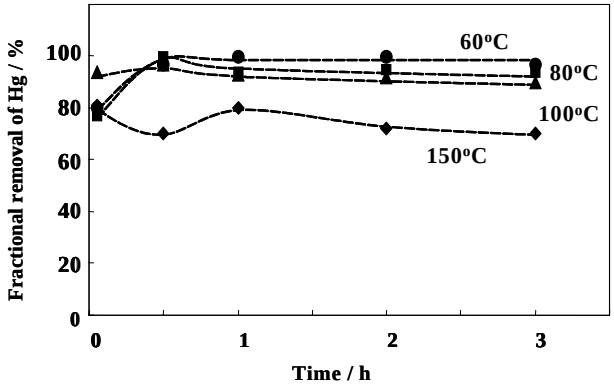

Figure 4. Effect of temperature on the Hg removal.

was increase when the used sample was exposed to the air. Furthermore, the sulfur smelled up from the sample at that time. After cooling in nitrogen atmosphere, another used sample was measured with XRD. We confirmed the formation of magnetite in the sample. From these results, it was suggested that the formed sulfur over the sample vaporized by heating when the sample magnetite exothermally changed to hematite with air. Form these experimental results and consideration, it was supposed that sulfur formed from H_2S over the iron oxide contributed to the Hg removal and also the surface oxygen or part of the lattice oxygen of the sample iron oxide contribute to produce of sulfur from H_2S.

Effect of the presence of CO and H_2Oon the Hg removal

As shown in **Figure 5**, the presence of CO at 150°C accelerated the Hg removal but the acceleration of the presence of it at 80oC was not observed. The effect of the presence of H_2 at 80°C also did not observed

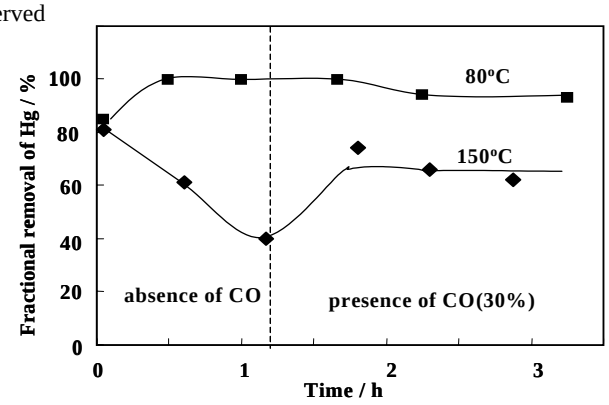

Figure 5. Effect of the presence of CO on the Hg removal

The presence of H_2O depressed the Hg removal in the temperature hole range from 60 to 150oC.

Conclusion

The characters of the Hg removal for the flue gas with the AC and the Hg removal for the fuel gas with the iron oxide could be considerably clarified.

Acknowledgment

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